SOFT MATERIALS FROM POLYELECTROLYTE-MULTIVALENT ION MIXTURES

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Aqueous mixtures of polyelectrolytes with multivalent counterions yield an array of functional soft materials, which range from micro- and nanoparticles to macroscopic gels and coacervates. These materials find use in diverse applications, including pharmaceutical, cosmetic and food formulations, wet adhesion, inorganic materials synthesis, and catalysis. To illustrate some of their notable properties, we will focus on two dissimilar types of such materials: (1) gels prepared through the ionic crosslinking of the cationic polysaccharide, chitosan; and (2) complex coacervates prepared via the ionotropic gelation of the synthetic, linear polycation, poly(allylamine hydrochloride) (PAH). When chitosan is mixed with pentavalent tripolyphosphate (TPP) anions, it is crosslinked into soft (storage moduli ~10^3–10^4 Pa) and water-rich gels which, depending on their preparation method, can either have colloidal or macroscopic dimensions. These chitosan/TPP gels, especially those with colloidal sizes (i.e., micro- and nanogels), have attracted widespread interest in biological applications, such as the delivery of drugs, genes and vaccines. To this end, we have examined the physicochemical effects underlying their formation, size distributions, stability, and drug uptake and release properties and, in the first part of this talk will describe how the formation, colloidal aggregation and size distributions of these particles are impacted by monovalent salt. The competitive binding of monovalent ions to the crosslink-forming ionic groups slows down chitosan/TPP micro- and nanogel formation, which both facilitates its mechanistic study and makes the particle formation process (and the final particle size distributions) easier to control. Once the particles are formed, the presence of monovalent salt slows down their aggregation in the presence of excess TPP by evidently preventing TPP adsorption to the particle surface and inhibiting bridging flocculation. Thus, monovalent salt addition can be utilized to control both chitosan/TPP micro- and nanogels size distributions and colloidal stability.

Conversely, when the polysaccharide chitosan is replaced with the more flexible and highly charged PAH, putty-like complex coacervates with storage moduli exceeding 10^5 Pa and much lower water contents form instead of the soft and water-rich gels. Unlike with their chitosan/TPP counterparts, coagulation of colloidal PAH/TPP complexes into macroscopic coacervate phases is accelerated by monovalent salt addition, which also (unlike its apparent effect on chitosan/TPP gels) noticeably accelerates coacervate relaxation. The PAH/TPP coacervates also adhere to both hydrophilic and hydrophobic surfaces (thus demonstrating their potential as wet adhesives), and can be dissolved on demand by changing the ambient pH. Moreover, the high crosslink densities within the adhesive PAH/TPP networks enable them to serve as vehicles for highly sustained release, where they can deliver a wide range of small molecule actives over multi-month timescales (which far exceed the < 1-day release times that are typically achieved with the chitosan/TPP system). Collectively, the disparate ionic network behaviors described in this talk will show the diverse range of properties that can be accessed with polyelectrolyte/multivalent ion mixtures, and highlight opportunities for further fundamental work in bridging the gap between their divergent characteristics.